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Conductivity of Monovalent Metals*

J. BARDEEN†
Harvard University, Cambridge, Massachusetts

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The conductivity of monovalent metals is computed from the Bloch theory under the assumption that the wave functions of the electrons are nearly the same as those of free electrons throughout the major part of the volume. The perturbation potential resulting from the Debye elastic waves, which produce transitions between the electronic states, is the sum of two terms: (1) the change in the total potential of the ions, which are assumed to move rigidly with the elastic waves, and (2) the change in the potential of the self-consistent field of the valence electrons. The second part tends to compensate the first. Scattering of electrons through angles greater than $2\sin^{-1}2^{-\frac{2}{3}}$ ($\sim$79°) results from the "*Umklappprozesse*" of Peierls. It is shown that the probability of these transitions joins smoothly with the probability of transitions of the ordinary type, so that the probability is a continuous function of the angle of deflection, and transitions through all angles are possible. Comparison with experiment is made through Bethe's interaction constant C, which is a measure of the average scattering power of the elastic waves. Table I gives the theoretical and experimental values of C/ζ, where ζ is the Fermi energy. Reasonable agreement is obtained for Na and K, but the theoretical values of C for the remaining monovalent metals are somewhat too small.

I. INTRODUCTION

THE modern quantum theory of the electrical conductivities of metals has been very successful in giving a qualitative, and in some cases a quantitative, explanation of such experimental results as the following: the Wiedemann-Franz law, the dependence of conductivity on temperature (in particular, the infinite conductivity at zero temperature), the effect of impurities, and the conductivities of solid solutions. It seems, however, to be very difficult to make an accurate calculation of the absolute value of the conductivity of a metal. The resistance of a pure metal results from the interaction of the electron waves with the lattice vibrations, and little is known about either the electronic wave functions or the frequency spectrum of the vibrations of most metallic crystals.

An attempt is made in the present paper to calculate the conductivity of a monovalent metal under the usual assumption that the wave functions of the electrons are nearly the same as those of free electrons throughout the major part of the volume. The Debye theory is used to obtain the frequency spectrum of the elastic waves. Our treatment differs from previous theories in two respects: (1) the perturbation resulting from the elastic waves, which is responsible for the transitions between the electronic states, is determined in a consistent manner by calculating the change in the self-consistent field of the valence electrons when the crystal is distorted, and (2) the probability of transitions resulting from the "*Umklappprozesse*" is determined. These latter transitions are responsible for the scattering of electrons through angles greater than $2\sin^{-1}2^{-\frac{2}{3}}$($\sim$79°).

The main outlines of the theory of conductivity are rather definite. According to Bloch,[1] the wave functions of the electrons moving in the periodic potential field of the undistorted crystal are of the form:

$$\psi(\mathbf{k})=\exp\left[i\mathbf{k}\cdot\mathbf{x}\right]U(\mathbf{k},\mathbf{x}), \tag{1}$$

where $U(\mathbf{k},\mathbf{x})$ has the translational period of the lattice. The configuration of the electrons may be described by giving the distribution of electrons in $\mathbf{k}$ space. If an electric field acts on the metal, the distribution of electrons will no longer by symmetric about the origin of $\mathbf{k}$ space, but will be displaced in the direction of the field. The new distribution results from an equilibrium between the transitions due to the field, and those due to the lattice vibrations. Bloch[1] obtained an integral equation for the new distribution by setting up the conditions for equilibrium. Due to mathematical difficulties, it has so far been possible to solve this equation only with the following simplifications:

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† Society of Fellows, Harvard University.

[1] F. Bloch, Zeits. f. Physik 52, 555 (1928).

(1) The energy of an electron in the state $\mathbf{k}$ is a function of $|\mathbf{k}|$, and is independent of the direction of $\mathbf{k}$.

(2) The probability of a transition from a state $\mathbf{k}$ to a state $\mathbf{k}'$ due to the lattice vibrations depends only on the angle between $\mathbf{k}$ and $\mathbf{k}'$ (or, equivalently, on $|\mathbf{k}-\mathbf{k}'|$).

These conditions are approximately satisfied only by the monovalent metals.[2]

The thermal motion of the ions is generally analyzed into a system of independent sound waves, after the manner of Debye. The displacement of an ion at the lattice point $\mathbf{R}_n$ is then of the form:

$$\delta\mathbf{R}_n=\Sigma(\mathbf{q}j)\{\mathbf{A}_{qj}\exp(i\mathbf{q}\cdot\mathbf{R}_n-i\omega_{qj}t)+\mathbf{A}_{qj}^*\exp(-i\mathbf{q}\cdot\mathbf{R}_n+i\omega_{qj}t)\},\quad(2)$$

in which $\mathbf{q}$ is the propagation vector, and ω_{qj} is the angular frequency of the wave. The index $j=(1, 2, 3)$ refers to the three possible directions of motion of the ions. Transitions between the electronic states are due to the displacement of the ions from their equilibrium positions.

A calculation of the probability of the transition $\mathbf{k}\rightarrow\mathbf{k}'$ due to the thermal motion of the ions depends on the evaluation of the matrix element:

$$M(\mathbf{kk}')=\int\psi(\mathbf{k}')^*V_p\psi(\mathbf{k})d\tau,\quad(3)$$

where V_p is the perturbation potential resulting from the lattice vibrations. Several different forms for V_p have been chosen by the authors who have discussed the subject. Bethe and Bloch[3] have used the hypothesis of a "deformable potential." If the potential at the point $\mathbf{r}$ in the undistorted crystal is $V(\mathbf{r})$, the potential at the same point in a crystal subject to the distortion $\delta\mathbf{r}$ is assumed to be $V(\mathbf{r}-\delta\mathbf{r})$, and V_p is then the difference between these, $V(\mathbf{r}-\delta\mathbf{r})-V(\mathbf{r})$. Nordheim[4] introduced the idea of a "rigid ion." If $v(\mathbf{r})$ is the potential of a single ion, the total potential of the ions is $\Sigma_n v(\mathbf{r}-\mathbf{R}_n)$. The ionic potential of the distorted lattice will then be $\Sigma_n v(\mathbf{r}-\mathbf{R}_n-\delta\mathbf{R}_n)$. Nordheim supposed that the perturbation potential, V_p, is the difference between these, and thus neglected the distortion in the electronic potential. Both of these hypotheses result in an interaction between electrons and lattice vibrations which is too large, and therefore in a value for the resistance which is much greater than the experimental value. Mott and Jones[5] assume that in each atomic cell, the potential is due entirely to the ion in the center of the cell. Then, in the nth cell, V_p is $v(\mathbf{r}-\mathbf{R}_n-\delta\mathbf{R}_n)-v(\mathbf{r}-\mathbf{R}_n)$. Due to the neglect of the potential of an ion outside of its own cell, they obtain a value for the resistance which is somewhat too small.

The most recent discussion of the subject is that of Peterson and Nordheim.[6] These authors object to the method discussed above of describing the effect of the lattice vibrations as a perturbation acting on the wave functions of the electrons in the undistorted crystal, because the perturbation potential and wave functions are both large in the neighborhood of the ions. An attempt is made to construct approximate wave functions of the progressive wave type for electrons in the distorted crystal, and transitions between these functions are considered. The method is applicable when the periodic part of the wave function of an electron in the undistorted crystal, $U(\mathbf{k},\mathbf{r})$, is reasonably independent of the propagation vector $\mathbf{k}$. For "starting" wave functions they take functions of the form $\exp[i\mathbf{k}\cdot\mathbf{r}]\,U_d(\mathbf{r})$ where $U_d(\mathbf{r})$ is the *exact* wave function of an electron in its lowest state in the *distorted* crystal. It is assumed that $(U_d(\mathbf{r}))^2$ is proportional to the electronic charge density. In order to obtain the charge density, it is assumed that the atomic cells are distorted by the lattice vibrations, and that the total electronic charge in each cell is equal to the charge of one ion. A knowledge of the perturbation potential is not required, as the matrix element required for the transition probability depends essentially on a Fourier component of the charge density, and is independent of the potential. Approximate agreement with the experimental

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[2] A discussion appropriate to divalent and transition metals, where two Brillouin zones are of importance, has been given by Mott, Proc. Roy. Soc. **A153**, 699 (1936).

[3] A. Sommerfeld and H. A. Bethe, *Handbuch der Physik*, Vol. 24, II (Berlin, 1933); Bloch, reference 1.

[4] L. W. Nordheim, Ann. d. Physik **9**, 607 (1931).

[5] N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Oxford, 1936). These authors use the Einstein model, instead of the Debye model, for the thermal motion, and so do not need to consider the "*Umklappprozesse*."

[6] E. L. Peterson and L. W. Nordheim, Phys. Rev. **51**, 355 (1937).

values of the resistances of Na and K is obtained, but these authors neglect transitions due to the "*Umklappprozesse*" of Peierls,[7] which would greatly increase the resistance if included.

Furthermore, the assumption concerning the form of U_d is not correct, as the density of electrons in the distorted crystal is not proportional to U_d^2. According to the theory of Peterson and Nordheim, the conductivity at low temperatures should be proportional to T^9 instead of T^5. The latter follows from the theory of Bloch, and is justified by experimental data (cf. Section 5).

While the general procedure of these authors is undoubtedly correct, we believe that the ordinary perturbation procedure is also correct as long as the displacement of the ions is small compared with the interatomic distance. If U_d is computed correctly, both methods should lead to the same result. Regions near the ions, where the perturbation is large, make a negligible contribution to the matrix element.[8]

The perturbation potential acting on a given electron consists of two parts: (1) the change in the potential of the ions[9] (which is given by the "rigid ion" hypothesis of Nordheim above) and (2) the change in the potential of the self-consistent field of the valence electrons. The second part tends to cancel the first. Let us consider the transitions due to a single elastic wave of wave number **q**. It is well known that the allowed transitions **k**→**k**′ are such that

$$\mathbf{k}-\mathbf{k}'=\pm\mathbf{q}+\mathbf{K}_n, \tag{4}$$

where $\mathbf{K}_n$ is a vector of the reciprocal lattice space, such that $\mathbf{K}_n\cdot\mathbf{R}_m$ is a multiple of 2π. Furthermore, we have the requirement of the conservation of energy:

$$E_{k'}=E_k\pm\hbar\omega_q. \tag{5}$$

The few electrons for which these conditions are satisfied do not contribute appreciably to the self-consistent field. The wave functions of the remaining electrons change adiabatically with the elastic waves. The field acting on an electron is the potential of the ions together with the adiabatically varying potential of the self-consistent field. The perturbation potential, V_p, is the difference between the fields in the distorted and the undistorted crystals.

A calculation of the self-consistent field is carried out in detail for a simple model in Section 3. It is assumed that the wave functions of the electrons in the undistorted crystal are sufficiently close to the plane wave functions, $\psi(\mathbf{k})=\exp\,[i\mathbf{k}\cdot\mathbf{r}]$ so that the latter may be used to determine the charge distribution. This requires that the periodic part of the actual wave function, $U(\mathbf{k},\,\mathbf{r})$, be fairly flat throughout the major part of the volume. The calculations of Wigner and Seitz and of Slater[10] show that this assumption is valid for Na, and it probably holds reasonably well for other monovalent metals as well.

It has been found possible to determine the probability of transitions resulting from the "*Umklappprozesse*" (values of $\mathbf{K}_n\neq 0$ in Eq. (4)). The probability is of the same order of magnitude as the probability of an ordinary transition and does not depend markedly on the direction of the propagation vector **k** of the initial state, so that the theory of Bloch may be applied. Transitions are possible for all angles between **k** and **k**′; the transitions through angles greater than $2\sin 2^{-\frac{2}{3}}$ ($\sim 79°$) are due to the "*Umklappprozesse.*"

II. General Theory of Conductivity

Reviews of the theory of conductivity as developed by Sommerfeld and Bloch may be found in many places in the literature,[11] so only the results we shall need later will be quoted here. For temperatures well above the characteristic temperature of Debye, the formula for the conductivity may be written in the Drude-Lorentz-Somerfeld form:

$$\sigma=(Ne^2/\hbar k_m)v_m\tau. \tag{6}$$

The notation is as follows: N is the number of

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[7] R. Peierls, Ann. d. Physik **12**, 154 (1932).

[8] Cf. reference 5, p. 254.

[9] It is assumed that the ions may be replaced by a central force field which follows the motion of the ions. This assumption is probably justified for the alkali metals, since the ionic radii are small compared with the interatomic distance; it is more questionable for the noble metals.

[10] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934); J. C. Slater, Phys. Rev. **45**, 794 (1934); Rev. Mod. Phys. **6**, 209 (1934).

[11] The recent books of Mott and Jones (reference 5), Frohlich, *Electronentheorie der Metalle* (Berlin, 1936), and Wilson, *The Theory of Metals* (Cambridge, 1936), may be found useful. The notation of the present paper follows more closely that of the older article of Sommerfeld and Bethe (reference 3).

valence electrons per unit volume, v_m is the group velocity of an electron in a state, k_m, at the top of the Fermi distribution, and τ is the mean lifetime of an electron in the state k_m. The value of τ, as determined from the integral equation of Bloch is given by

$$(1/\tau)=(k_m{}^2/\pi\hbar)(dk/dE)_m\int_0^\pi |M(\mathbf{kk}')|^2 \times(1-\cos\theta)\sin\theta d\theta; \quad (7)$$

where θ is the angle between $\mathbf{k}$ and $\mathbf{k}'$. In the derivation of (7), it has been assumed that E is a function of $|\mathbf{k}|$, and that $M(\mathbf{kk}')$ is a function of $|\mathbf{k}-\mathbf{k}'|$. The matrix element is defined by (1).

In computing the matrix element, one may suppose that the elastic waves with different wave numbers scatter independently. Since the motion of the ions is slow compared with that of the electrons, it is possible to consider the scattering of a stationary wave. The displacement of the ion at the point $\mathbf{R}_n$ due to an elastic wave of wave number $\mathbf{q}$ is

$$\delta\mathbf{R}_n=N^{-\frac{1}{2}}\mathbf{n}_q(a_q\exp[i\mathbf{q}\cdot\mathbf{R}_n] +a_q{}^*\exp[-i\mathbf{q}\cdot\mathbf{R}_n]), \quad (8)$$

where $\mathbf{n}_q$ is a unit vector in the direction of motion of the ions, and N is the number of atoms per unit volume. At high temperatures, $T\gg\Theta$ the amplitude of the vibration is given by:

$$|a_q|^2=\kappa T/2M\omega_q{}^2, \quad (9)$$

where κ is the Boltzmann constant, M is the mass of the atom, and ω_q is the angular frequency of the vibration. According to the elementary treatment of Debye, the frequency is given by

$$\omega_q=qc, \quad (10)$$

where c is the velocity of the wave, which is assumed to be independent of $\mathbf{q}$ and of the direction of motion of the ions. The maximum value of $\mathbf{q}$ may be expressed in terms of Θ, the Debye characteristic temperature:

$$\hbar q_m=\hbar(6\pi^2N)^{\frac{1}{3}}=\kappa\Theta/c. \quad (11)$$

While the Debye treatment is not very accurate, one is almost forced to use it in the present stage of the theory, because little is known about the actual frequency spectrum of metallic crystals. Furthermore, Bloch's integral equation has not yet been solved for the general case.

At low temperatures ($T<\Theta$), the sound waves must be quantized, and the energy of the sound quantum may no longer be neglected in comparison with κT. A brief discussion of the conductivity at low temperatures is given in Section 5.

III. Calculation of the Matrix Element

We consider the scattering due to a single elastic wave of wave number $\mathbf{q}$, defined by (8) above. The perturbation potential, V_p, resulting from this wave is the sum of two terms: V_i, the change in potential of the ions, and V_ρ, the change in the potential of the self-consistent field of the valence electrons. Since the amplitude of the vibration is small, it is possible to determine V_ρ by a perturbation procedure in which terms of higher order than the first in the amplitude are neglected. For V_i we have simply:

$$V_i=-N^{-\frac{1}{2}}a_q\Sigma_m\exp[i\mathbf{q}\cdot\mathbf{R}_m]\mathbf{n}_q\cdot\text{grad}\, v(\mathbf{r}-\mathbf{R}_m)+\text{comp. conj.} \quad (12)$$

The potential $v(\mathbf{r})$ is the potential of a single ion, and the sum runs over all N ions in the unit volume.

It is more difficult to compute the potential V_ρ which results from the modification of the electronic charge distribution. In order to simplify the calculation, we assume that the wave functions of the electrons in the undistorted crystal run close to the free electron wave functions, $\psi^0(\mathbf{k})=\exp[i\mathbf{k}\cdot\mathbf{r}]$ throughout most of the volume. The self-consistent field is computed by a perturbation procedure in which the wave functions of the electrons in the distorted crystal are expanded in terms of the wave functions of the electrons in the undistorted crystal.

If we expand $V_i\psi(\mathbf{k})$ in terms of the wave functions, $\psi(\mathbf{k}')$, of the electrons in the undistorted crystal, the only values of $\mathbf{k}'$ which enter are those which satisfy condition (4) above. Thus,

$$V_i\psi(\mathbf{k}) = \Sigma_n\{ V_{in+}\psi(\mathbf{k}+\mathbf{q}+\mathbf{K}_n) + V_{in-}\psi(\mathbf{k}-\mathbf{q}-\mathbf{K}_n)\}, \tag{13}$$

where the sum is over all points of the reciprocal lattice space, and

$$V_{in+} = \int \psi(\mathbf{k}+\mathbf{q}+\mathbf{K}_n)^* V_i\psi(\mathbf{k})d\tau = -N^{-\frac{1}{2}}a_q\int \exp\left[-i(\mathbf{q}+\mathbf{K}_n)\cdot\mathbf{r}\right] \times\{\Sigma_m \exp\left[i\mathbf{q}\cdot\mathbf{R}_m\right]\mathbf{n}_q\cdot\operatorname{grad} v(\mathbf{r}-\mathbf{R}_m)\}\, U(\mathbf{k}+\mathbf{q}+\mathbf{K}_n)^* U(\mathbf{k})d\tau. \tag{14}$$

Interchanging the order of summation and integration, we have, after summation over m,

$$V_{in+} = -N^{-\frac{1}{2}}a_q\int \exp\left[-i(\mathbf{q}+\mathbf{K}_n)\cdot\mathbf{r}\right]\mathbf{n}_q\cdot\operatorname{grad} v(\mathbf{r})\, U(\mathbf{k}+\mathbf{q}+\mathbf{K}_n)^* U(\mathbf{k})d\tau. \tag{15}$$

The integration is throughout space. We have made use of the fact that $U(\mathbf{k})$ is periodic. There is a similar expression for V_{in-}. In the approximation of nearly free electrons, V_{in} is independent of the propagation vector $\mathbf{k}$ of the initial state.

The wave functions, $\Psi(\mathbf{k})$, of the electrons in the distorted crystal may be expanded in a similar series,

$$\Psi(\mathbf{k}) = \psi(\mathbf{k}) + \Sigma_m\{b(\mathbf{k}n+)\psi(\mathbf{k}+\mathbf{q}+\mathbf{K}_n) + b(\mathbf{k}n-)\psi(\mathbf{k}-\mathbf{q}-\mathbf{K}_n)\}. \tag{16}$$

In computing the charge density and potential resulting from these wave functions, we assume that $\psi(\mathbf{k})$ for the undistorted crystal is approximately,

$$\psi(\mathbf{k}) = \exp\left[i\mathbf{k}\cdot\mathbf{n}\right]U_0(\mathbf{r}) \tag{17}$$

and that $U_0(\mathbf{r})$ is flat throughout most of the volume.

The density of electrons is, to the first order,

$$\rho = \Sigma(\mathbf{k})\Psi(\mathbf{k})^*\Psi(\mathbf{k}) = \rho_0 + \Sigma(\mathbf{k}, n)\, U_0{}^2\{(b(\mathbf{k}n+) + b(\mathbf{k}n-)^*) \exp\left[i(\mathbf{q}+\mathbf{K}_n)\cdot\mathbf{r}\right] + (b(\mathbf{k}n+)^* + b(\mathbf{k}n-)) \exp\left[-i(\mathbf{q}+\mathbf{K}_n)\cdot\mathbf{r}\right]\}, \tag{18}$$

where ρ_0 is the density of electrons in the undistorted crystal. The summation over $\mathbf{k}$ is over all occupied states.

From the equation,

$$\Delta V_\rho = -4\pi e^2(\rho - \rho_0), \tag{19}$$

we may determine the change is the electrostatic potential of the electrons resulting from the distortion of the crystal. We make the further approximation that $U_0{}^2 \backsimeq 1$, so that (19) may be easily integrated. This approximation should be satisfactory for the terms in which we are interested; i.e., those for which $\mathbf{q}+\mathbf{K}_n$ is small. To this approximation, the potential is:

$$V_\rho = \Sigma_n\{ V_{\rho n} \exp\left[i(\mathbf{q}+\mathbf{K}_n)\cdot\mathbf{r}\right] + V_{\rho n}{}^* \exp\left[-i(\mathbf{q}+\mathbf{K}_n)\cdot\mathbf{r}\right]\}, \tag{20}$$

where

$$V_{\rho n} = 4\pi e^2|\mathbf{q}+\mathbf{K}_n|^{-2}\Sigma(\mathbf{k})(b(\mathbf{k}n+) + b(\mathbf{k}n-)^*). \tag{21}$$

The $b(\mathbf{k}n)$ are to be determined from the Schrödinger equation,

$$-(\hbar^2/2m)\Delta\Psi(\mathbf{k}) + (V_0 + V_i + V_\rho)\Psi(\mathbf{k}) = E(\mathbf{k})\Psi(\mathbf{k}), \tag{22}$$

where V_0 is the total potential, ionic plus electrostatic, in the undistorted crystal. The energy of an electron is unchanged in the first order by the distortion of the crystal. In the free electron approximation,

$$E_k = E_0 + \hbar^2 k^2/2m. \tag{23}$$

Substituting (13), (16) and (20) in Eq. (22), and keeping only first-order terms, we obtain the following set of equations for the $b(\mathbf{k}n)$:

$$\begin{aligned}(E(\mathbf{k}+\mathbf{q}+\mathbf{K}_n)-E(\mathbf{k}))b(\mathbf{k}n+)+V_{in+}+V_{\rho n}=0,\\ (E(\mathbf{k}-\mathbf{q}-\mathbf{K}_n)-E(\mathbf{k}))b(\mathbf{k}n-)+V_{in-}+V_{\rho n}^*=0.\end{aligned} \tag{24}$$

These equations serve to determine the $b(\mathbf{k}n)$ except for $\mathbf{k}$ such that

$$E(\mathbf{k})\sim E(\mathbf{k}+\mathbf{q}+\mathbf{K}_n);\quad E(\mathbf{k})\sim E(\mathbf{k}-\mathbf{q}-\mathbf{K}_n); \tag{25}$$

when the simple perturbation procedure breaks down. It is, of course, just these $\mathbf{k}$ for which transitions are possible. Solving (24), we find

$$\begin{aligned}b(\mathbf{k}n+)=(V_{in+}+V_{\rho n})(E(\mathbf{k})-E(\mathbf{k}+\mathbf{q}+\mathbf{K}_n))^{-1},\\ b(\mathbf{k}n-)=(V_{in-}+V_{\rho n}^*)(E(\mathbf{k})-E(\mathbf{k}-\mathbf{q}-\mathbf{K}_n))^{-1}.\end{aligned} \tag{26}$$

The $V_{\rho n}$ still involve the $b(\mathbf{k}n)$. An equation for $V_{\rho n}$ may be obtained by substituting the values of $b(\mathbf{k}n)$ given by (26) into (21). Some care must be taken in carrying out the summation over $\mathbf{k}$, because the $b(\mathbf{k}n)$ become large for certain values of $\mathbf{k}$. It will be convenient to define an average energy, $W(\mathbf{q}+\mathbf{K}_n)$ which is a function of $|\mathbf{q}+\mathbf{K}_n|$ to be determined below, by

$$[W(\mathbf{q}+\mathbf{K}_n)]^{-1}=N^{-1}\Sigma(\mathbf{k})(E(\mathbf{k}+\mathbf{q}+\mathbf{K}_n)-E(\mathbf{k}))^{-1}, \tag{27}$$

so that we have the following equation for $V_{\rho n}$:

$$V_{\rho n}=-(V_{in+}+V_{\rho n})(8\pi e^2N)|\mathbf{q}+\mathbf{K}_n|^{-2}[W(\mathbf{q}+\mathbf{K}_n)]^{-1}. \tag{28}$$

Solving, we obtain

$$V_{\rho n}=-V_{in+}(1+(8\pi e^2N)^{-1}|\mathbf{q}+\mathbf{K}_n|^2[W(\mathbf{q}+\mathbf{K}_n)])^{-1}. \tag{29}$$

In our approximation, the matrix element, $M(\mathbf{k}\mathbf{k}')$, corresponding to the transition $\mathbf{k}\rightarrow\mathbf{k}'=\mathbf{k}+\mathbf{q}+\mathbf{K}_n$ is:

$$M(\mathbf{k}\mathbf{k}')=V_{in+}+V_{\rho n}=V_{in+}(1+8\pi e^2N|\mathbf{q}+\mathbf{K}_n|^{-2}[W(\mathbf{q}+\mathbf{K}_n)]^{-1})^{-1}. \tag{30}$$

The factor multiplying V_{in+} is a measure of the compensation of the distortion of the ionic potential by the shift in the charge density of the valence electrons. For elastic waves of long wave-length ($\mathbf{q}$ small, $\mathbf{K}_n=0$) the compensation is almost complete; the compensation is less effective for waves of shorter wave-length.

There remains to determine $W(\mathbf{q}+\mathbf{K}_n)$ from from (27) and V_{in} from (15). The summation over $\mathbf{k}$ in (27) may be replaced by an integration over the occupied states in $\mathbf{k}$ space. We introduce cylindrical coordinates (ζ, ρ, α), in $\mathbf{k}$ space, with the axis in the direction of $\mathbf{K}\equiv\mathbf{q}+\mathbf{K}_n$. From a consideration of the behavior of the $b(\mathbf{k}n)$ for those values of $\mathbf{k}$ for which (24) is satisfied, it is easily shown that the integral we require is:

$$[W(\mathbf{K})]^{-1}=\lim_{\epsilon\rightarrow 0}\frac{3m}{\hbar^2k_m^3}\left\{\int_{-k_m}^{-(K/2)-\epsilon}\frac{d\zeta}{[(K+\zeta)^2-\zeta^2]}\int_0^{(k_m^2-\zeta^2)^{\frac{1}{2}}}\rho d\rho+\int_{-(K/2)+\epsilon}^{k_m}\frac{d\zeta}{[(K+\zeta)^2-\zeta^2]}\int_0^{(k_m^2-\zeta^2)^{\frac{1}{2}}}\rho d\rho\right\}. \tag{31}$$

We have used (23) for E_k. The integration may easily be carried out by elementary methods, and we find:

$$W(\mathbf{K})=\frac{4}{3}\frac{\hbar^2k_m{}^2}{2m}\left\{\frac{1}{2}+\frac{4k_m{}^2-K^2}{8k_mK}\log\frac{2k_m+K}{2k_m-K}\right\}^{-1}. \tag{32}$$

In calculating V_{in} from (15), it will be convenient to divide the integration over space into two parts: the integration over the central cell, and the integration over the remainder of space. The former may be transformed into a surface integral; the latter may be simplified by the approximations $U(\mathbf{k})\simeq 1$; $v(\mathbf{r})\simeq -e^2/r$. In carrying out the integration, we replace the central cell by a sphere of equal volume (radius r_s). We then have

$$V_{in+}=-N^{\frac{1}{2}}a_q(I_1+I_2), \tag{33}$$

with

$$\begin{aligned} I_1&=\int_{\text{cell}}\exp\left[-i(\mathbf{q}+\mathbf{K}_n)\cdot\mathbf{r}\right]\mathbf{n}_q\cdot\operatorname{grad} v(r)\,U(\mathbf{k}+\mathbf{q}+\mathbf{K}_n)^*U(\mathbf{k})d\tau,\\ I_2&=-\int_{r_s}^{\infty}\int_0^{2\pi}\int_0^{\pi}\exp\left[-i(\mathbf{q}+\mathbf{K}_n)\cdot\mathbf{r}\right]\mathbf{n}_q\cdot\operatorname{grad}(e^2/r)d\tau. \end{aligned} \tag{34}$$

By elementary methods, we find:

$$\begin{aligned} I_2&=4\pi e^2\cos(\mathbf{n}_q,\mathbf{q}+\mathbf{K}_n)\int_{r_s}^{\infty}\int_0^1 u\sin(|\mathbf{q}+\mathbf{K}_n|ru)du\,dr\\ &=-(4\pi ie^2/|\mathbf{q}+\mathbf{K}_n|)\cos(\mathbf{n}_q,\mathbf{q}+\mathbf{K}_n)(\sin x/x), \end{aligned} \tag{35}$$

where

$$x=|\mathbf{q}+\mathbf{K}_n|r_s. \tag{36}$$

In any cell, the undistorted potential V_0 is approximately equal to the potential of the ion in the center of the cell plus the potential of the electron cloud within the cell, since the potential of the ions in neighboring cells is very nearly cancelled by the potential of the electrons in those cells. The potential of the electron cloud, with the assumption of uniform density, is equal to $(3e^2/2r_s)-(e^2r^2/2r_s{}^3)$. We thus have

$$V_0(r)=v(r)+(3e^2/2r_s)-(e^2r^2/2r_s{}^3). \tag{37}$$

The integral I_1 is then,

$$\begin{aligned} I_1=\int_{\text{cell}}\psi(\mathbf{k}')^*\mathbf{n}_q\cdot\operatorname{grad} v(r)\psi(\mathbf{k})d\tau&=\int_{\text{cell}}\psi(\mathbf{k}')^*\mathbf{n}_q\cdot\operatorname{grad} V_0\psi(\mathbf{k})d\tau\\ &+\int_{\text{cell}}\psi(\mathbf{k}')^*\mathbf{n}_q\cdot\operatorname{grad}(e^2r^2/2r_s{}^3)\psi(\mathbf{k})d\tau. \end{aligned} \tag{38}$$

The first integral on the right-hand side of (38) may be transformed into a surface integral which is rather small in magnitude; the second may easily be evaluated directly.

According to Mott and Jones,[12]

$$\int_{\text{cell}}\psi(\mathbf{k}')^*\mathbf{n}_q\cdot\operatorname{grad} V_0\psi(\mathbf{k})d\tau=(\hbar^2/2m)\mathbf{n}_q\cdot\int\left[\psi(\mathbf{k}')^*(\partial/\partial n)\operatorname{grad}\psi(\mathbf{k})-\operatorname{grad}\psi(\mathbf{k})(\partial/\partial n)\psi(\mathbf{k}')^*\right]dS, \tag{39}$$

the second integral being over the surface of the cell. With the approximation of nearly free electrons,

$$\psi(\mathbf{k})\simeq\exp\left[i\mathbf{k}\cdot\mathbf{r}\right]U_0(r);\quad U_0(r_s)\simeq 1;\quad U'(r_s)=0; \tag{40}$$

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[12] Reference 5, p. 253.

it is easily shown that the surface integral is equal to:

$$-4\pi i r_s^2 \cos(\mathbf{n}_q, \mathbf{q}+\mathbf{K}_n)(V_0(r_s)-E_0)(\sin x - x\cos x)/x^2, \tag{41}$$

where E_0 is the energy of an electron in its lowest state. The potential in each cell is given by (37), and the wave function of an electron in its lowest state satisfies the Schrödinger equation,

$$-(\hbar^2/2m)\Delta U + V_0 U = E_0 U. \tag{42}$$

It should be noted that E_0 includes the Coulomb energy, which, for free electrons is $1.2e^2/r_s$. The values of E_0 should be quite small for most monovalent metals. Since $v(r) \backsimeq -e^2/r$, $V_0(r_s) \backsimeq 0$.

In the second integral on the right-hand side of (38), we may set with sufficient accuracy, $\psi(\mathbf{k}) = \exp[i\mathbf{k}\cdot\mathbf{r}]$ so that

$$\int_{\text{cell}} \psi(\mathbf{k}')^* \mathbf{n}_q \cdot \text{grad}\,(e^2r^2/2r_s^3)\psi(\mathbf{k})d\tau = \int_{\text{cell}} \exp[-i(\mathbf{q}+\mathbf{K}_n)\cdot\mathbf{r}]\mathbf{n}_q\cdot\text{grad}\,(e^2r^2/2r_s^3)d\tau. \tag{43}$$

Integration by elementary methods gives the following value for the integral:

$$-(4\pi i e^2/|\mathbf{q}+\mathbf{K}_n|)\cos(\mathbf{n}_q, \mathbf{q}+\mathbf{K}_n)[3(\sin x - x\cos x) - x^2 \sin x]/x^3. \tag{44}$$

From (35), (41), and (44), we have, finally,

$$I_1+I_2 = -\frac{i|\mathbf{q}+\mathbf{K}_n|}{N}\left(\frac{4\pi e^2 N}{|\mathbf{q}+\mathbf{K}_n|^2} + V_0(r_s) - E_0\right)\cos(\mathbf{n}_q, \mathbf{q}+\mathbf{K}_n)\left(\frac{3(\sin x - x\cos x)}{x^3}\right) \tag{45}$$

and $M(\mathbf{kk}')$ may easily be obtained from (30) and (33). An explicit expression will be given in the next section.

IV. Calculation of the Conductivity

The reciprocal mean lifetime, $1/\tau$, is to be obtained by expressing the matrix element $M(\mathbf{kk}')$ as a function of the angle of scattering, θ, and then integrating over all angles from 0 to π, as indicated by Eq. (7). For the transitions of interest, we must satisfy the conservation of energy, which, in our approximation, gives

$$k'^2 = |\mathbf{k}+\mathbf{q}+\mathbf{K}_n|^2 = k^2,$$

$$\text{or} \qquad |\mathbf{q}+\mathbf{K}_n|^2 = -2\mathbf{k}\cdot(\mathbf{q}+\mathbf{K}_n). \tag{46}$$

Given any $\mathbf{k}$ and $\mathbf{k}'$ such that $k^2 = k'^2$, one can always choose $\mathbf{q}$ and $\mathbf{K}_n$ in such a way that (46) is fulfilled. If the angle θ between $\mathbf{k}$ and $\mathbf{k}'$ is less than $2\sin^{-1} 2^{-\frac{2}{3}}(\sim 79°)$, $\mathbf{K}_n = 0$. For angles greater than 79°, one must take the $\mathbf{K}_n$ which connect the nearest neighbors to the origin of the reciprocal lattice space (these transitions correspond to the "*Umklappprozesse*" of Peierls). In order that the Bloch theory may be applied, the matrix element $M(\mathbf{kk}')$ must be independent of the direction of $\mathbf{k}$, and depend only on the angle between $\mathbf{k}$ and $\mathbf{k}'$, which may be expressed in terms of $|\mathbf{q}+\mathbf{K}_n|$. This requirement is satisfied if $\mathbf{K}_n = 0$. All the factors in $M(\mathbf{kk}')$ are functions of $|\mathbf{q}+\mathbf{K}_n|$ except a_q, which is a function of q. According to (10) and (11), a_q is inversely proportional to q. For most transitions resulting from the "*Umklappprozesse,*" q is quite large, and is close to its maximum value, q_m. We will therefore set $q = q_m$ in a_q for those transitions for which $\mathbf{K}_n \neq 0$, and thus underestimate the resistance to some extent. The theory of Bloch may then be applied in its usual form.

In order to simplify the equations, the following notation will be introduced:

$$\begin{aligned}
u &= \sin(\theta/2); \\
|\mathbf{q}+\mathbf{K}_n|^2 &= 2k_m^2(1-\cos\theta) = 4k_m^2u^2; \\
f(u) &= \tfrac{1}{2} + ((1-u^2)/4)\log((1+u)/(1-u)); \\
\xi(u) &= \begin{cases} 1, & u < 2^{-\frac{2}{3}} \\ 2^{\frac{2}{3}}u, & u > 2^{-\frac{2}{3}}; \end{cases} \\
g(u) &= 3(\sin x - x\cos x)/x^3; \\
x &= |\mathbf{q}+\mathbf{K}_n|r_s = 2k_m r_s u = 3.84u; \\
\zeta &= \hbar^2 k_m^2/2m; \\
\beta &= e^2 k_m/\pi\zeta.
\end{aligned} \tag{47}$$

Using (30), (32), (33), (45) and (47), and summing over the three directions of motion of the ions, we find, after some reduction, that

$$\Sigma(\mathbf{n}_q)\,|M(u)|^2=(4/9N)\,|\mathbf{q}a_q|^2(G(u))^2, \qquad (48)$$

where

$$G(u)=g(u)\xi(u)[1+(Vr_s)-E_0)(3u^2/\beta\zeta)] \times[f(u)+(2/\beta)u^2]^{-1}\zeta. \qquad (49)$$

As u approaches zero (deflection through small angles) the factor multiplying ζ in (49) approaches unity. As u increases, $G(u)$ decreases, and becomes rather small when $u=1$ (deflection through an angle of 180°). It is to be noted that there is no discontinuity in $G(u)$ at $u=2^{-\frac{2}{3}}(\theta\sim 79°)$. The probability of transitions due to the "*Umklappprozesse*" joins smoothly with the probability of transitions of the ordinary type.

The reciprocal mean lifetime is obtained by substituting (48) into (7). The integration over θ is changed to an integration over u, and we have

$$(1/\tau)=2^{-5/3}(k_m{}^2/\pi\hbar)(dk/dE)_m \times(4/9N)\,|qa_q|^2C^2, \qquad (50)$$

in which it has been convenient to introduce a mean square value of $G(u)$ defined by

$$C^2=4u_m{}^{-4}\int_0^1(G(u))^2u^3du =2^{14/3}\int_0^1(G(u))^2u^3du, \qquad (51)$$

where $u_m=2^{-\frac{2}{3}}$ is the maximum value of u for an ordinary transition. As thus defined, C is the interaction constant of Sommerfeld and Bethe.[13]

We may simplify (50) to some extent by use of (9), (10), and (11). The substitution for $|qa_q|^2$ gives, after some reduction,

$$(1/\tau)=\hbar^2\pi^3Nk_m{}^{-2}(dk/dE)_m(T/M\kappa\Theta^2)C^2. \qquad (52)$$

The conductivity is obtained by substitution of (52) into (6):

$$\sigma=Me^2(\hbar\pi)^{-3}k_m(dE/dk)_m{}^2(\kappa\Theta^2/T)C^{-2}, \qquad (53)$$

which is Eq. (36.11) of Sommerfeld and Bethe.

As the characteristic temperatures are not known accurately for most of the monovalent metals, it is perhaps best to compare the directly calculated quantity with the experimental values of σ/Θ^2, which may be expressed in terms of the interaction constant C^2. If we use the free electron value for E, we have

$$k_m(dE/dk)_m=2\zeta. \qquad (54)$$

Eq. (53) may then be written in the form

$$(\zeta/C)^2=\pi\sigma mhT/4\beta M\kappa\Theta^2. \qquad (55)$$

Table I gives a comparison of the experimental and theoretical values of C/ζ for the monovalent metals. The relevant data for the calculation of C/ζ from the experimental values of σ and Θ are also given. As the characteristic temperatures of the alkalis are rather uncertain, two values have been given for Na and K. The lower values are those of Fuchs[14] as derived from the specific heat at low temperatures; the higher values are those of Gruneisen[15] as obtained from the variation of conductivity with temperature. The former values are perhaps to be preferred, because the theory of conductivity at intermediate temperatures is rather uncertain. Row (8) of Table I

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[13] Reference 3, p. 513.

[14] K. Fuchs, Proc. Roy. Soc. **A153**, 622 (1936).

[15] Gruneisen, Ann. d. Physik **16**, 530 (1933).

TABLE I. *Comparison of the experimental and theoretical values of C/ζ for the monovalent metals.*

1	METAL	Na	K	Rb	Cs	Cu	Ag	Au
2	Atomic Wgt.	23	39	85.5	133	63.6	108	197
3	$\sigma(\Omega^{-1}\ \mathrm{cm}^{-1};\ 0°\mathrm{C})$	22.6	15.3	8.2	5.4	64	67	68
4	Θ	150–202	100–126	~85	~55	315	215	175
5	$r_s\times 10^8$	2.12	2.56	2.81	3.13	1.41	1.58	1.58
6	β	1.33	1.60	1.77	1.9	0.89	1.00	1.00
7	C/ζ (exp)	0.77–1.04	0.87–1.10	1.6	1.65	1.32	1.21	1.30
8	C/ζ (theor.*)	0.72	0.77	0.80	0.82	0.61	0.64	0.64
9	$V_0(r_s)-E_0$ (ev)	0.2				1.3	1.1	(3.7)
10	C/ζ (theor.)	0.77				0.80	0.83	0.90

* Assuming that $V_0(r_s)-E_0=0$.

gives the theoretical values of C/ζ, computed under the assumption that $V_0-E_0=0$. This assumption should be very nearly correct for the alkalis (except Li). Row (9) gives the theoretical values of E_0 for Na, Cu and Ag as determined from the work of Wigner and Seitz[10] and of Fuchs.[16] The value given for Au was estimated from the ionization potential and the heat of sublimation. It should be noted that the theoretical values of C/ζ for all the metals listed are close to 0.8, and are thus very close to the theoretical values of Peterson and Nordheim[6] (0.84 for all monovalent metals). Since we have underestimated the effect of "*Umklappprozesse,*" the true theoretical values should be larger (by perhaps ten or fifteen percent).

The agreement obtained for Na and Rb is satisfactory, but the calculated values for the noble metals and for Rb and Cs are somewhat too small. It is perhaps not surprizing that the values for the noble metals are too low, because our assumptions are very likely not justified for these metals, but one would expect closer agreement for Rb and Cs in view of the fact that many properties of these metals can be explained on the assumption of free electron wave functions.

The accuracy that can be expected from the one-electron picture on which the Bloch theory is based is uncertain. The effect of electron exchange on the conductivity will be discussed by the author in a forthcoming paper.

V. Conductivity at Low Temperatures

At low temperatures ($T\ll\Theta$), the only elastic waves which will be excited are those with small wave number $\mathbf{q}$, and the electrons can be scattered only through small angles. The theory has been discussed by Bloch[1] with the following simplifying assumptions:

(1) Debye theory for eastic waves,
(2) Thermal equilibrium of elastic waves,
(3) $E(\mathbf{k})$ a function of $|\mathbf{k}|$ alone,
(4) $G(u)=\text{constant}$,
(5) Neglect of "*Umklappprozesse.*"

If T_1 and T_2 are two temperatures such that

$$T_1\ll\Theta\ll T_2 \tag{56}$$

and σ_1 and σ_2 are the corresponding conductivities, it was shown that

$$\sigma_2/\sigma_1=497.6(T_1/\Theta)^4(T_1/T_2). \tag{57}$$

According to the present theory, the numerical factor will be slightly different. As θ (or u) approaches zero, $G(u)$ approaches ζ. It is easily seen that (57) must be multiplied by ζ^2/C^2, so that we have

$$\sigma_2/\sigma_1=497.6(\zeta^2/C^2)(T_1/\Theta)^4(T_1/T_2). \tag{58}$$

For Na, the numerical factor is increased by a factor of about 1.6. Gruneisen has shown that the T^5 law is obeyed by most metals at low temperatures, but it is difficult to estimate the numerical factor from experimental data because of the uncertainty in Θ, which enters in a high power.

The criticism of Peierls[7] of the theory of conductivity at low temperatures must not be forgotten. It is difficult to see how the elastic waves in a monovalent metal can be in thermal equilibrium when a current is flowing.

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[16] K. Fuchs, Proc. Roy. Soc. **A151**, 585 (1935).